

Diffuse soil CO₂ flux to assess the reliability of CO₂ storage in the Mazarrón–Gañuelas Tertiary Basin (Spain)

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ABSTRACT

In the framework of a global investigation of the Spanish natural analogues of CO₂ storage and leakage, four selected sites from the Mazarrón–Gañuelas Tertiary Basin (Murcia, Spain) were studied for computing the diffuse soil CO₂ flux, by using the accumulation chamber method. The Basin is characterized by the presence of a deep, saline, thermal (~47 °C) CO₂-rich aquifer intersected by two deep geothermal exploration wells named “El Saladillo” (535 m) and “El Reventón” (710 m).

The CO₂ flux data were processed by means of a graphical–statistical method, kriging estimation and sequential Gaussian simulation algorithms. The results have allowed concluding that the Tertiary marly cap-rock of this CO₂-rich aquifer acts as a very effective sealing, preventing any CO₂ leak from this natural CO₂ storage site, being therefore an excellent scenario to guarantee, by analogy, the safety of a CO₂ storage.

1. Introduction

Carbon dioxide is a greenhouse gas (GHG) that naturally exists in the atmosphere. Anthropogenic activities, especially those related to the power generation from fossil fuels, are causing the increase of this gas concentration in the atmosphere since the industrialisation era that began in the early XIX century [1], and it is predicted to increase further. This phenomenon likely contributes to the known and worldwide accepted climate change.

One of the most important options to reduce CO₂ emissions to the atmosphere is the development of Carbon Capture and Storage technologies (CCS), which have been mainly deployed into large industrial emission sources, such as power and cement plants, refineries, steelworks and ceramic industries. These technologies firstly involve the separation of the CO₂ from the rest of the gases emitted by such emission sources. Later on, it is compressed to obtain a concentrated stream of CO₂. Finally, it is transported and injected into a suitable geological storage formation in a depth greater than 800 m, where CO₂ reaches the supercritical state. Therefore, the CO₂ deep geological storage represents the last stage

of CCS technologies and, what is more important, the most internationally accepted method for CO₂ sequestration, in order to minimize the effects on the global climatology.

Among the possible deep geological storage formations, deep saline aquifers are apparently the most suitable options, particularly in those countries where other options, such as gas and oil depleted or *quasi* depleted reservoirs, as well as non-mining coal seams, are not viable. In Spain, the estimated capacity of geological CO₂ storage in deep saline aquifers is about 45,000 Mton, according to data from the EU GeoCapacity Project [2].

However, in order to provide robust predictions of the performance of CO₂ disposal sites at the required timescale (>1000 a), the study of natural CO₂ accumulation sites is required [3,4], since they are powerful tools to understand the long-term behaviour of the CO₂ once injected into the suitable geological formation.

The scientific community has indeed generally accepted that long-term extrapolation in terms of safety of a deep geological storage of toxic industrial wastes (high activity radioactive wastes, industrial and mining wastes) and even greenhouse gases cannot be satisfactorily realized on the basis of short-term laboratory investigations [5]. Therefore, countries affected by these problems have developed methods of investigation, which include both laboratory tests, where the variables are controlled, and the study of industrial and natural analogues.

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Although investigations on natural CO₂-rich accumulation systems are not yet sufficiently developed, some authors [6,7] have listed the existing CO₂ natural reservoirs worldwide and the experimental reactions between CO₂ and the storage formations [8]. Moreover, in the last decade several studies have focused their attention on the evaluation of the safety of a CO₂ geological storage by investigating CO₂ natural analogues [9–17].

In this respect, one of the most important aspects concerning the performance assessment of a deep CO₂ geological repository in a deep saline aquifer is to increase the knowledge on the interaction among CO₂ and the storage and sealing formations, as well as the physico-mechanical resistance of the sealing formation. As a consequence, the measurements of the surficial CO₂ leakage rates are an important tool to evaluate: (i) the efficiency of the aforementioned interaction processes; (ii) the capacity of the sealing geological formation for the retention of CO₂; and (iii) the possible effects of the CO₂ released on the environment.

For these reasons, this work is focused on the retention capacity of the cap-rock by measuring the diffuse soil CO₂ flux in a selected site, according to: (i) the presence of a deep CO₂-rich saline aquifer; (ii) the structural geological characteristics; and (iii) the nature of the cap-rock. This site is located in the Mazarrón-Gañuelas Tertiary Basin, which it is in the southeast of the Iberian Peninsula, inside the Internal Zones of the Betic Cordillera (Fig. 1).

The deep CO₂-rich saline aquifer is hosted in an important marble formation and discovered through geothermal investigations carried out in the 1980s [18]. The cap-rock is formed by Tertiary marls (>500 m thick), that avoided the CO₂ leakages until irrigation wells were drilled in the 1960s. The over-exploitation of the shallowest fresh aquifers caused their contamination by the deep-seated CO₂. In addition, CO₂ might be released through leakage paths represented by the main faults.

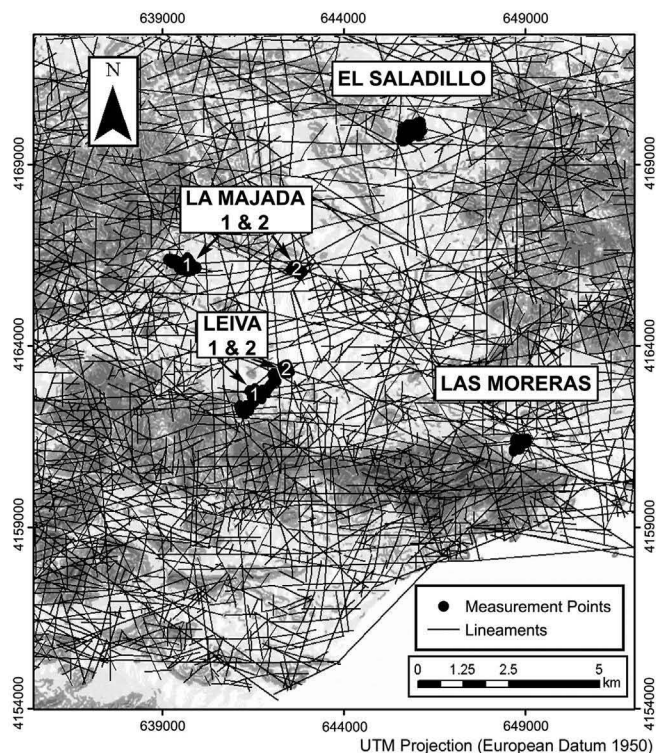


Fig. 2. Location map of the explored sites. Notice the high lineament intersection density existing in these sites.

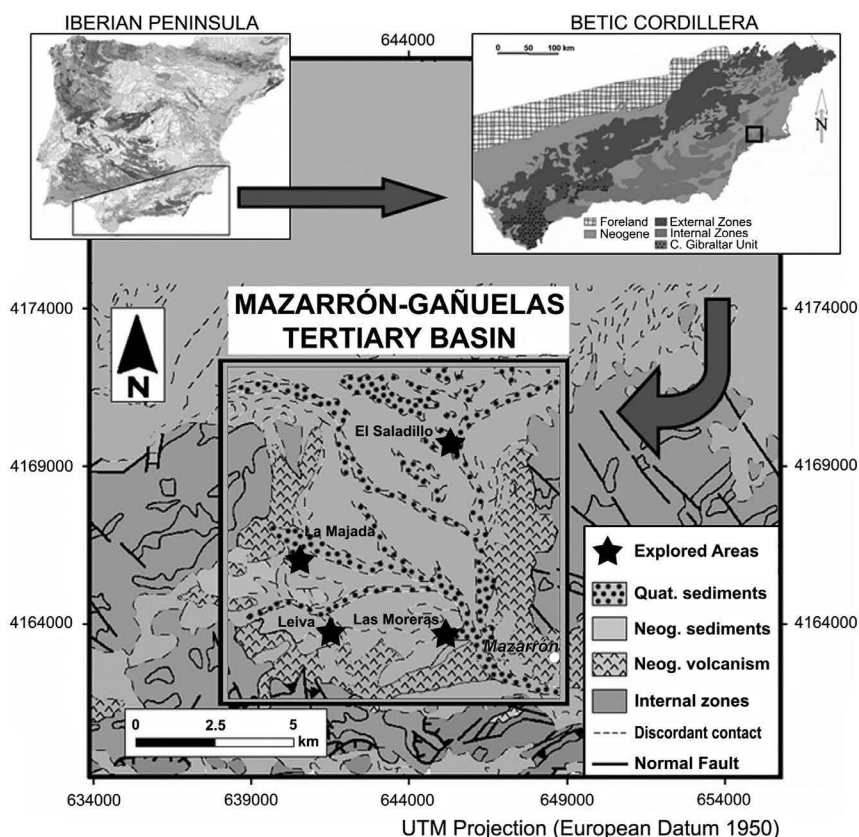


Fig. 1. Schematic geological map of the Mazarrón-Gañuelas Tertiary Basin.

Table 1
Location, number of diffuse CO₂ flux measurements and total explored surface.

Sites	Measurements	Explored surface (m ²)
El Saladillo	187	136000
Las Moreras	128	52,700
La Majada (1 & 2)	370	125,800
Leiva (1 & 2)	351	209,600

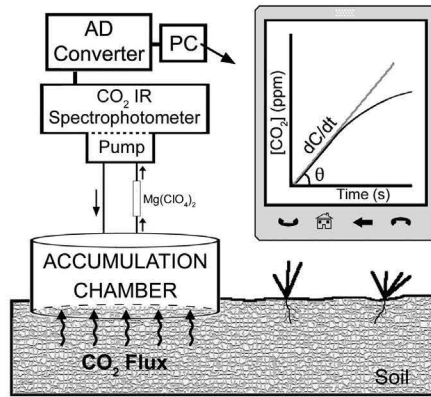


Fig. 3. Schematic representation of the accumulation chamber method used in the measurements of the diffuse soil CO₂ flux, modified from [31].

Therefore, though CO₂ was detected after drilling wells for irrigation and geothermal purposes, the main objective of this work was the detection of the possible CO₂ leakages from the deep saline aquifer, in order to:

- Determine whether the cap-rock (marly formation) is able to act as an effective and efficient geological sealing to CO₂.
- Extrapolate the results, by analogy, to predict the long-term behaviour of the sealing materials of an artificial deep geological CO₂ storage.

2. Materials and methods

The diffuse soil CO₂ flux was measured in sites previously selected according to their geological features, and particularly on

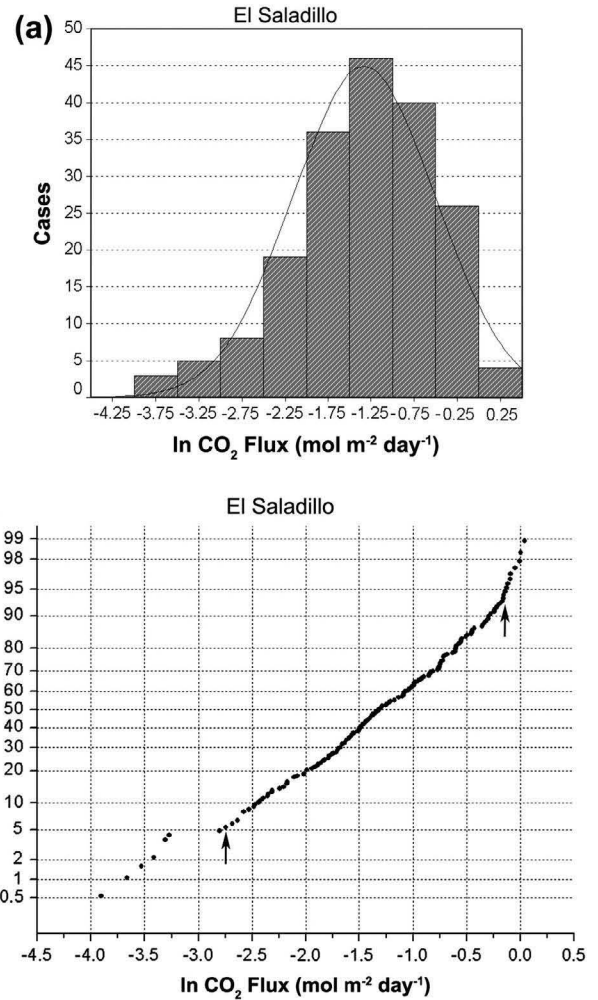


Fig. 4. Histogram (a) and probability plots (b) corresponding to lnCO₂ flux, expressed in mol m⁻² day⁻¹, for El Saladillo site. Note the Gaussian distribution of the measurements population. The inflection points are indicated by arrows.

the basis of the density of the lineament intersections since they should likely correspond to preferential leakage paths for the deep-seated CO₂ [19,20]. For this purpose, a lineament (probable

Table 2
Basic descriptive statistical parameters obtained from CO₂ flux measurements, expressed in mol m⁻² day⁻¹ and g m⁻² day⁻¹.

El Saladillo (Sept. 2009)	Measurements	Average	Min	Max	Standard deviation
CO ₂ Flux (mol m ⁻² day ⁻¹)	187	0.353	0.020	1.103	0.254
CO ₂ Flux (g m ⁻² day ⁻¹)	187	15.53	0.887	48.541	11.188
Las Moreras (September 2009)					
CO ₂ Flux (mol m ⁻² day ⁻¹)	128	0.261	0.008	0.929	0.195
CO ₂ Flux (g m ⁻² day ⁻¹)	128	11.475	0.333	40.874	8.582
La Majada (September 2009)					
CO ₂ Flux (mol m ⁻² day ⁻¹)	277	0.877	0.007	7.503	0.787
CO ₂ Flux (g m ⁻² day ⁻¹)	277	38.584	0.322	330.149	34.635
La Majada (March 2010)					
CO ₂ Flux (mol m ⁻² day ⁻¹)	93	0.499	0.033	1.425	0.338
CO ₂ Flux (g m ⁻² day ⁻¹)	93	21.958	1.469	62.693	14.861
Leiva (September 2009)					
CO ₂ Flux (mol m ⁻² day ⁻¹)	257	0.394	0.025	1.491	0.238
CO ₂ Flux (g m ⁻² day ⁻¹)	257	17.333	1.091	65.597	10.455
Leiva (March 2010)					
CO ₂ Flux (mol m ⁻² day ⁻¹)	94	0.354	0.042	1.447	0.254
CO ₂ Flux (g m ⁻² day ⁻¹)	94	15.569	1.837	63.673	11.175

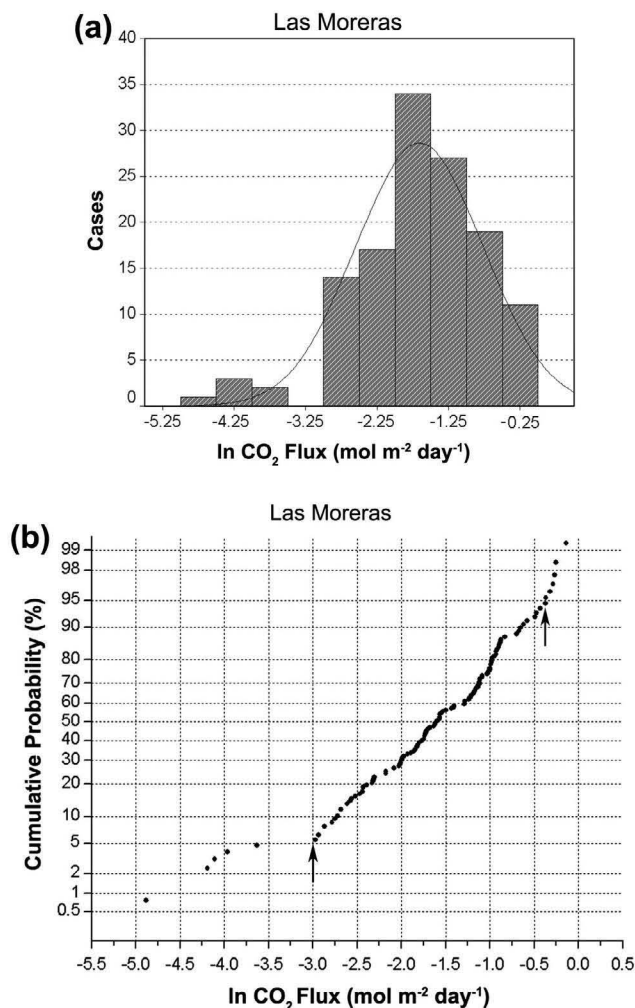


Fig. 5. Histogram (a) and probability plots (b) corresponding to $\ln \text{CO}_2$ Flux, expressed in mol m⁻² day⁻¹, for Las Moreras site. Note the Gaussian distribution of the measurements population. The inflection points are indicated by arrows.

fractures and/or faults) study on orthophotographs of the site (Spanish Aerial Orthophoto Programme) is shown in Fig. 2. The studied sites, the surface areas and the number of measurements are reported in Table 1. These sites were explored during September 2009 and March 2010.

Geologically, Las Moreras, La Majada and Leiva sites are approximately located on the contact between the Tertiary materials from the Mazarrón-Gañuelas Basin and the Triassic surrounding mountains, whilst El Saladillo site is on the North boundary of the Basin (see Fig. 2). In this site, a deep well (535 m) was drilled during 1985 for geothermal exploration, which intersected a deep, high salinity (conductivity ~ 10 mS cm⁻¹), thermal (~ 47 °C) and CO_2 -rich aquifer. This aquifer is the only source of the free and dissolved CO_2 in the aforementioned Tertiary Basin. According to the $\delta^{13}\text{C}$ of the free CO_2 from El Saladillo and El Reventón wells (-10.15 and -0.38 , respectively) and the R/R_a (0.71) values (where R is the measured $^3\text{He}/^4\text{He}$ ratio and R_a is that of the air, i.e. 1.39×10^{-6}), the CO_2 in this Tertiary Basin seems to be a mixture of: (i) a CO_2 from thermometamorphic processes affecting deep carbonate formations; (ii) biogenic CO_2 ; and (iii) a deep-seated CO_2 of likely mantle origin [21–23].

The measurements campaigns were performed during dry and meteorologically stable periods, in order to avoid the possible influence of rainfalls and soil humidity. Environmental conditions

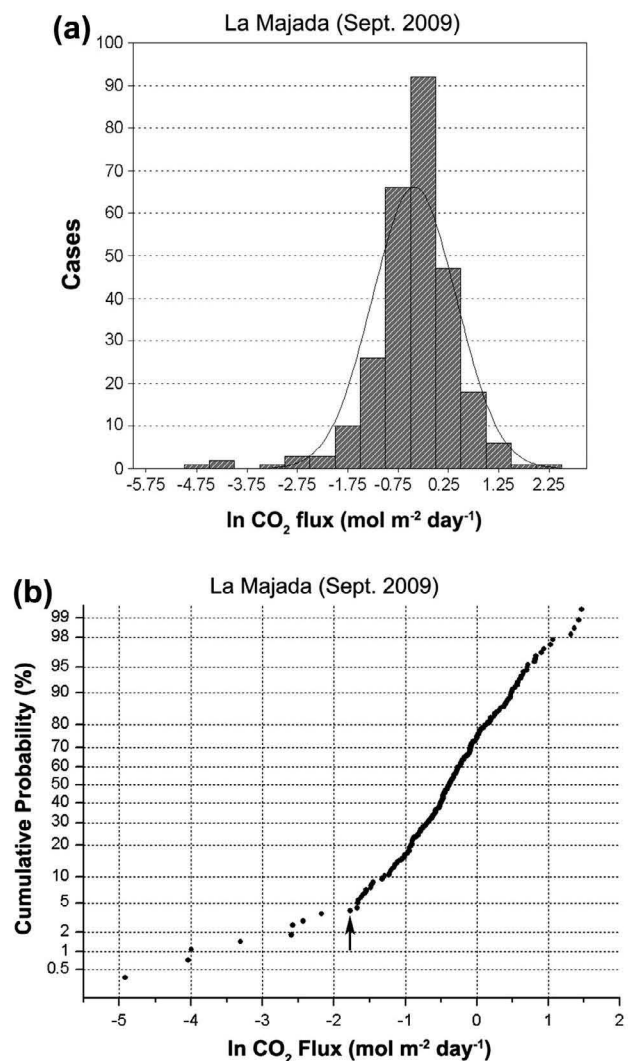


Fig. 6. Histogram (a) and probability plots (b) corresponding to $\ln \text{CO}_2$ flux, expressed in mol m⁻² day⁻¹, for La Majada site (September 2009). Note the Gaussian distribution of the measurements population. The inflection point is indicated by an arrow.

indeed strongly affect the soil CO_2 fluxes, since this gas is relatively soluble in water and, therefore, significantly affecting the CO_2 flux measurements.

CO_2 flux was performed by means of the accumulation chamber method [24–30], which is characterised by its sensitivity, low cost, fast and simple operability. Though this method was firstly used for agriculture purposes [27–30], in the last twenty years numerous studies focused on the diffuse CO_2 degassing in volcanic and geothermal environments were carried out [31–37]. Furthermore, this methodology is also applicable for monitoring gas emissions from landfills [38,39].

The equipment used is licensed by West Systems© Company and it includes: (i) an inverted chamber, with known dimensions, equipped with a system to mix the air in the chamber headspace; (ii) an Infra-Red (IR) Spectrophotometer, with a LICOR Li-820 sensor, (iii) an Analogical-Digital (AD) converter; and (iv) a Palmtop Computer (PC) (Fig. 3). A magnesium perchlorate desiccant trap is inserted between the outlet fitting of the accumulation chamber and the inlet of the tube connected to the pump, in order to prevent damages to both the pump and the CO_2 IR detector by soil humidity.

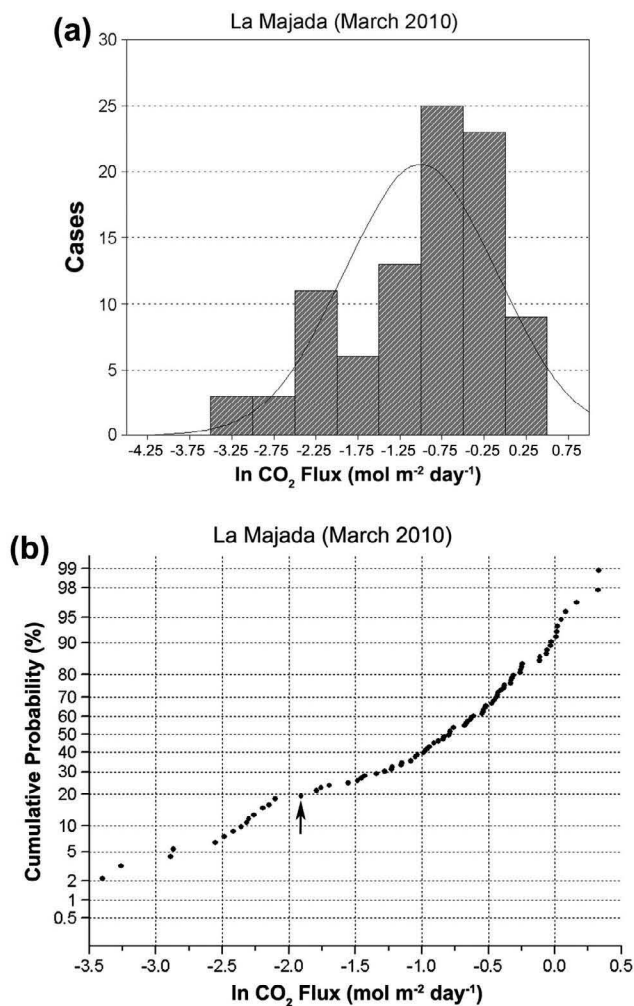


Fig. 7. Histogram (a) and probability plots (b) corresponding to $\ln \text{CO}_2$ flux, expressed in mol m⁻² day⁻¹, for La Majada site (March 2010). Note the Gaussian distribution of the measurements population. The inflection point is indicated by an arrow.

The method consists of placing the accumulation chamber above the soil surface, allowing the accumulation of the gas from soils. Then, the gas is pumped towards the CO_2 IR detector, at an approximate flow rate of 20 mL s⁻¹. Later on, the gas is returned to the camera, closing the circuit. Thus, the disturbances of the gas naturally released from the soil are minimized. Finally, the signal emitted by the IR is transformed by the AD converter and transmitted directly to the PC, where it is observed, in real time, the $[\text{CO}_2]$ versus time. Therefore, the flux is derived by obtaining the increase of the $[\text{CO}_2]$ as a function of time, expressed as ppm s⁻¹, in volume. In order to convert the volumetric concentration into mass concentration units (g m⁻² day⁻¹ or mol m⁻² day⁻¹), atmospheric pressure and temperature, both obtained during the field-work, and the chamber volume, are taken into account [40].

Computation of the total CO_2 output values was performed on the basis of a graphical-statistical analysis [31,33,41], by using SPSS and ORIGIN codes. This method, commonly used in the treatment of geochemical data, consists in the partition of the CO_2 flux values in different log-normal populations. For that, the inflection points were taken into account. On a log-probability plot, a single log-normal population results as a straight line, whilst a curve with an inflection point describes the theoretical distribution of two overlapped log-normal populations. In general, n overlapped

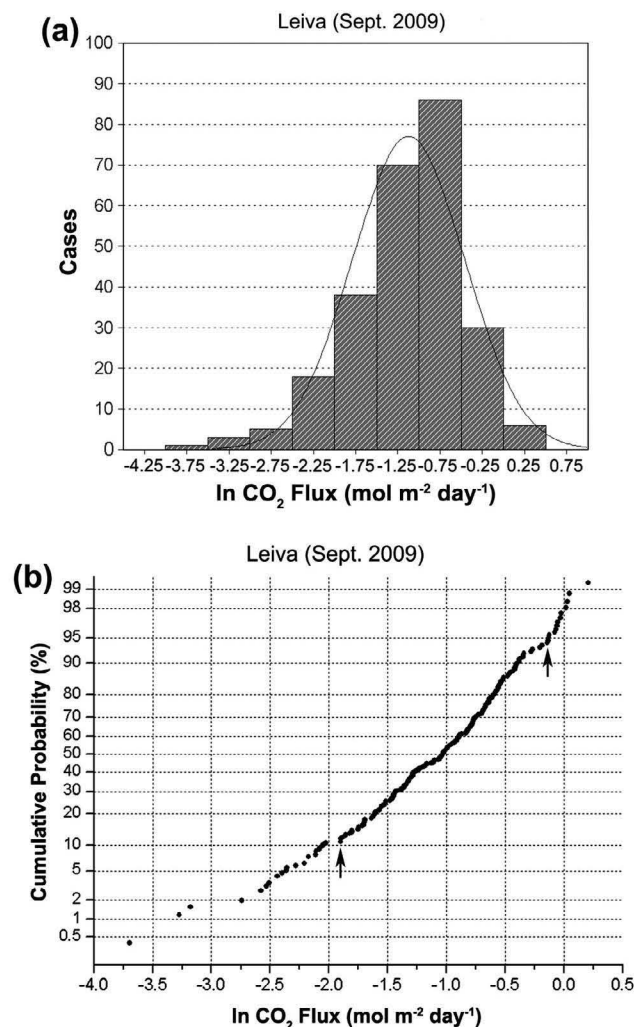


Fig. 8. Histogram (a) and probability plots (b) corresponding to $\ln \text{CO}_2$ flux, expressed in mol m⁻² day⁻¹, for Leiva site (September 2009). Note the Gaussian distribution of the measurements population. The inflection points are indicated by arrows.

log-normal populations result on a curve characterized by $n - 1$ inflection points [42]. Consequently, this method allows recognising the different populations from a data set. The necessary parameters to calculate the total CO_2 flux of each population was determined by using the Sichel method [43]. These parameters include the flux average values of the populations and their corresponding standard deviations.

It was used the graphical procedure according to since it allows the determination of the parameters necessary for the calculation of the total CO_2 flux, such as: (i) the estimation of the proportion of each observed population; (ii) the flux average value; and (iii) the standard deviation of each population.

The total CO_2 output associated with each population was obtained by multiplying the area of the measured site, the proportion of each population and the average CO_2 flux value. The average CO_2 flux values and the central 95% confidence interval of the average, which was used to calculate the uncertainty of the total CO_2 output estimated, were calculated by using the Sichel's t -estimator [32,43]. The total CO_2 released from the whole explored area was obtained by adding the contribution of each individual population.

Mapping of CO_2 flux spatial distribution in the explored areas was obtained by using both kriging estimation and sequential Gaussian simulation (sGs) geostatistical methods [44]. The CO_2 flux

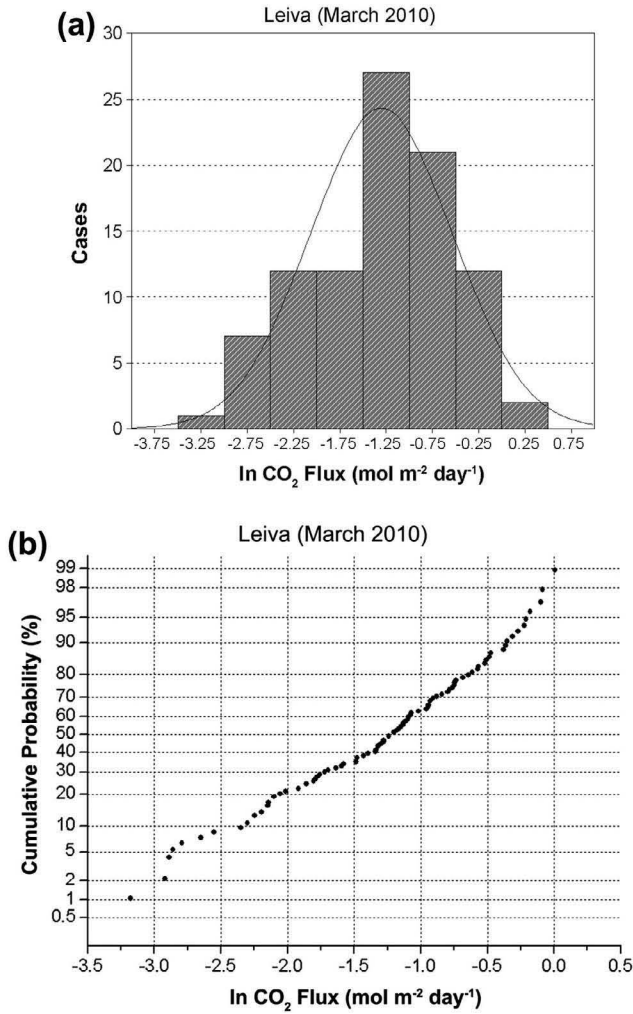


Fig. 9. Histogram (a) and probability plots (b) corresponding to $\ln \text{CO}_2$ flux, expressed in $\text{mol m}^{-2} \text{day}^{-1}$, for Leiva site (March 2010). Note the Gaussian distribution of the measurements population.

graphical representation was computed by combining the ArcGIS and Stanford Geostatistical Modeling Software (SGeMS) codes.

Kriging procedure provides a single map of the Best Linear Unbiased Estimator (BLUE) for quantities that vary in space. The estimates are “smoothed” such that low values are overestimated, whilst high values tend to be underestimated. This effect of smoothing is greatest in areas furthest from sample locations. However, the geostatistical simulation avoids some of the restrictions of kriging, since it does not aim to minimize local error variances. The basic idea of this stochastic simulation is the generation of equiprobable representations of the spatial distribution of the simulated values, reproducing the statistical (histogram) and spatial (variogram) characteristics of the original data [40,41]. The differences among all simulated maps (usually from 100 up to 500 realizations are performed) are used to compute the uncertainty of the CO_2 flux estimation. The sGs method was already widely used for the estimation of the soil CO_2 degassing at other volcanic systems [33,40,41,45–47].

Therefore, a simulated map looks more “realistic” than the map of the statistically “best” estimates, because it reproduces the spatial variability from the sample information [48].

3. Results and discussion

Data obtained during the two experimental campaigns were firstly treated by means of a statistical analysis, in order to calculate the basic statistic parameters (Table 2).

According to data reported in Table 2, it is worthy to note that CO_2 fluxes higher than $1 \text{ mol m}^{-2} \text{day}^{-1}$ was only sporadically recorded, La Majada being the site where the highest values were measured.

As the CO_2 flux data tend to a log-normal distribution, the $\ln(\text{CO}_2)$ flux data were processed according to the Sinclair method [42]. The log-probability plots allow the identification of the different populations for each explored site by means of the inflection points. For El Saladillo (Fig. 4) and Las Moreras (Fig. 5) sites two inflection points (-0.17 and -2.74 and -3.0 and -0.35 , respectively) were identified and, therefore, three populations were recognized. At La Majada site only one inflection point (-1.74) and two populations were observed in September 2009 (Fig. 6). For

Table 3

Estimated parameters of the different populations for each explored site and total CO_2 output, according to Sinclair method [42] and Sichel's t -estimator [43].

Explored Sites (Campaign)	CO_2 Flux Populations	Measurements	Proportion (%)	CO_2 Flux average (M_i) ($\text{mol m}^{-2} \text{day}^{-1}$)	Total CO_2 output (ton day^{-1})	95% Confidence interval standard deviation (ton day^{-1})
El Saladillo (September 2009)	1	13	7.0	0.876	0.365	0.373–0.361
	2	164	87.7	0.312	1.640	1.853–1.481
	3	10	5.3	0.036	0.012	0.029–0.007
	Total	187	100.0		2.018	2.254–1.849
Las Moreras (September 2009)	1	11	8.6	0.737	0.147	0.161–0.139
	2	111	86.7	0.231	0.466	0.527–0.420
	3	6	4.7	0.017	0.002	0.003–0.001
	Total	128	100.0		0.615	0.691–0.561
La Majada [1] (September 2009)	1	268	96.8	0.573	2.121	2.424–1.897
	2	9	3.2	0.011	0.001	0.006–0.001
	Total	277	100.0		2.122	2.430–1.898
La Majada [2] (March 2010)	1	78	83.9	0.482	0.695	0.806–0.618
	2	15	16.1	0.059	0.016	0.026–0.012
	Total	93	100.0		0.712	0.832–0.630
Leiva [1] (September 2009)	1	14	5.4	0.887	0.383	0.394–0.376
	2	213	82.9	0.378	2.481	2.666–2.334
	3	30	11.7	0.090	0.083	0.106–0.070
	Total	257	100.0		2.947	3.166–2.780
	1	94	100.0	0.359	0.475	0.572–0.408
Leiva [2] (March 2010)	Total	94	100.0		0.475	

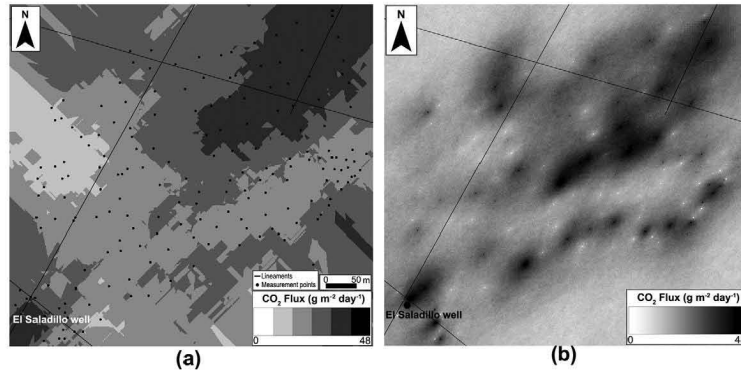


Fig. 10. (a) Surficial distribution of the diffuse soil CO₂ flux, in g m⁻² day⁻¹, for El Saladillo site, by means of a kriging estimation. (b) Sequential Gaussian simulation of the surficial CO₂ flux.

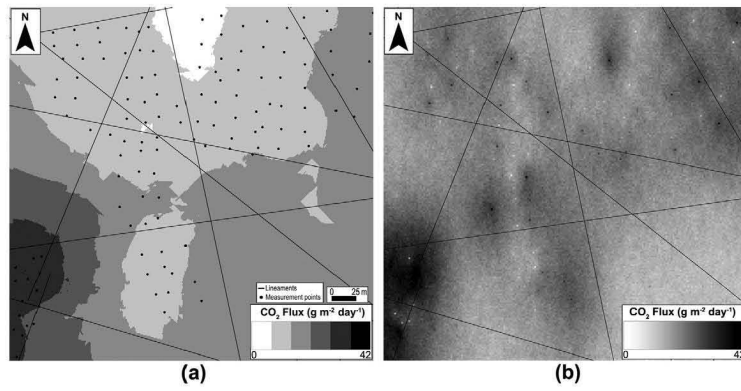


Fig. 11. (a) Surficial distribution of the diffuse soil CO₂ flux, in g m⁻² day⁻¹, for Las Moreras site, by means of a kriging estimation. (b) Sequential Gaussian simulation of the surficial CO₂ flux.

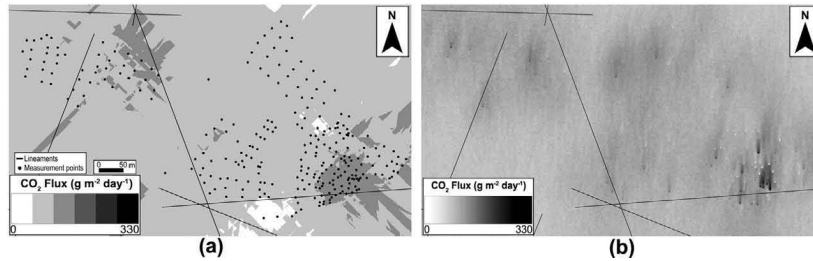


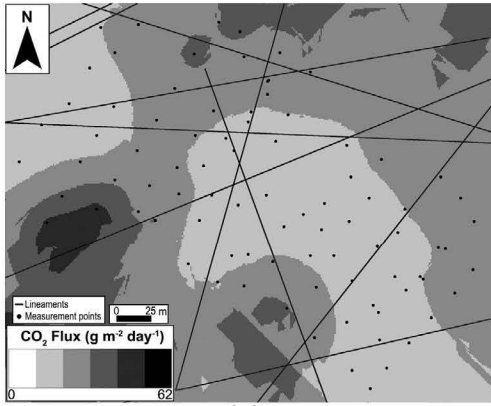
Fig. 12. (a) Surficial distribution of the diffuse soil CO₂ flux, in g m⁻² day⁻¹, for La Majada site (Sept. 2009), by means of a kriging estimation. (b) Sequential Gaussian simulation of the surficial CO₂ flux.

the same site two populations were identified in March 2010 (Fig. 7), being the inflection point at -1.90 . Finally, at Leiva site the coexistence of three populations (inflections points at -1.91 and -0.13) were observed in September 2009 (Fig. 8), whilst no individual populations (straight line) were recognized in March 2010 (Fig. 9). The populations that included few data, as it occurred in all the sites, except at Leiva site in March 2010, can be considered negligible when compared to the whole frequency distribution. Consequently, the main data set can be modelled along with the main population, that it can be evaluated as the “local background of CO₂ Flux”. The statistical parameters of the deduced populations are reported in Table 3.

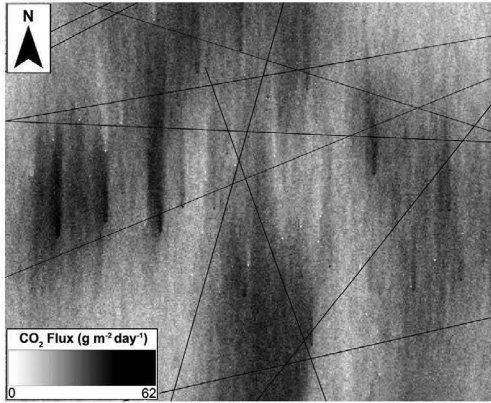
According to Sichel's t -estimator (M_i), the total amount of CO₂ released towards the surface is estimated to be 2.018, 0.615, 2.122, 0.712, 2.947 and 0.475 ton day⁻¹ for El Saladillo, Las Moreras, La Majada (September 2009 and March 2010) and Leiva

(September 2009 and March 2010) sites, respectively. By comparing these data with other sites, where CO₂ output is important, such as in some areas at Tuscany (Italy) occur (bubbling pools, dry vents and CO₂ soil degassing) [31,32], it can be estimated that the CO₂ output released from the explored sites is relatively low and similar to the typical biological CO₂ released from soils [49], which was estimated in approximately 5 g m⁻² day⁻¹ for arid environments [50]. However, the estimated CO₂ released from soils at Las Moreras site is about 11.67 g m⁻² day⁻¹, which is the minimum CO₂ output from the explored sites in this work. This value is more than two times the abovementioned biological CO₂ flux from arid soils. This difference can be explained considering that the studied zone is under semi-arid conditions, where some vegetation is developed.

As previously mentioned, the tools used for mapping the CO₂ surficial flux were the kriging estimation and sGs simulation meth-



(a)



(b)

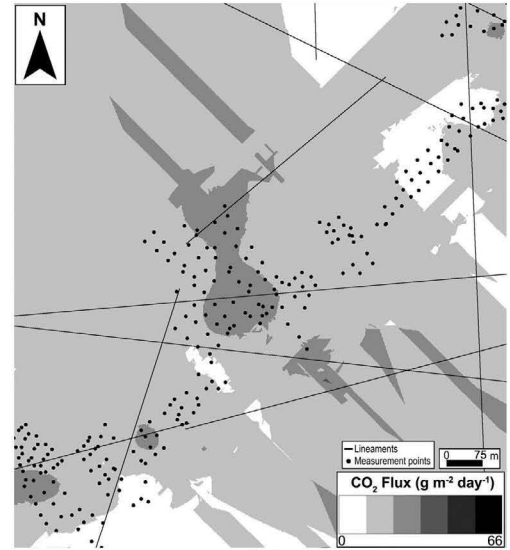
Fig. 13. (a) Surficial distribution of the diffuse soil CO_2 flux, in $\text{g m}^{-2} \text{day}^{-1}$, for La Majada site (March 2010), by means of a kriging estimation. (b) Sequential Gaussian simulation of the surficial CO_2 flux.

ods [44]. In principle, the relationships between the potential degassing channel (lineaments, faults and/or human perturbations) and the CO_2 flux values can be established observing the CO_2 map produced by both methods. However, no evident relationships between lineaments and CO_2 flux were observed in any site (Figs. 10–15). The exception is El Saladillo site, where a clear correspondence between human perturbation (El Saladillo well) and the CO_2 flux values exists (see Fig. 10). Consequently, in undisturbed sites no CO_2 leakages were evidenced, suggesting that the Tertiary marly formation, filling the Mazarrón–Gañuelas Basin, acts as a very effective sealing rock.

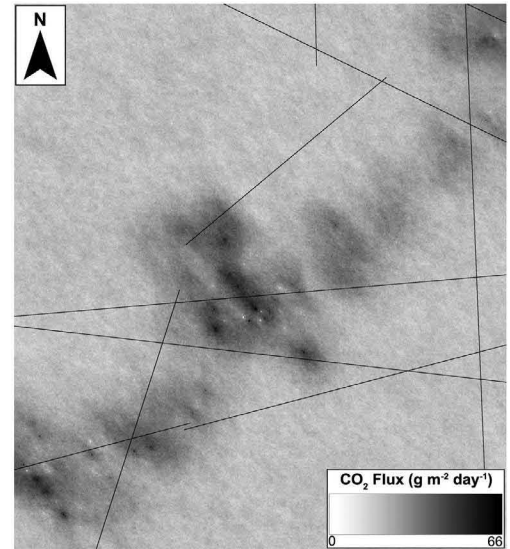
Finally, when both the kriging estimation and the sequential Gaussian simulation maps are compared, it is observed that they are very similar. Consequently, both methods are valid for the surficial CO_2 flux mapping and CO_2 quantification by interpolating/extrapolating of the measured values. Nevertheless, no clear correlations between structural discontinuities (lineaments) and higher CO_2 flux values were observed. On the contrary, close relationship between anthropogenic disturbances and higher CO_2 fluxes exists in El Saladillo site (see Fig. 10), where a deep exploration well was drilled.

4. Conclusions

On the basis of the diffuse soil CO_2 degassing surveys carried out in the Mazarrón–Gañuelas Tertiary Basin, some general conclusions can be outlined, as follows:



(a)



(b)

Fig. 14. (a) Surficial distribution of the diffuse soil CO_2 flux, in $\text{g m}^{-2} \text{day}^{-1}$, for Leiva site (September 2009), by means of a kriging estimation. (b) Sequential Gaussian simulation of the surficial CO_2 flux.

1. The cap-rock appears to be very efficient as sealing formation, since it does not allow any relevant CO_2 leakages towards the surface (up to $2.947 \text{ ton day}^{-1}$). That is, in terms of CO_2 soil flux, the Tertiary marly sedimentary deposits represent an impervious formation through which the escape of CO_2 is not jeopardized.
2. Both kriging estimation and sequential Gaussian simulation maps can be applied to the surficial CO_2 flux mapping and CO_2 quantification by interpolating/extrapolating the measured values in any similar sedimentary Basin.
3. The investigated sites have generally low CO_2 background and basically comparable to that observed in cultivated areas worldwide. However, some exceptions were detected in relation to anthropogenic perturbation and, to a lesser extent, to structural weakness or fault zones.

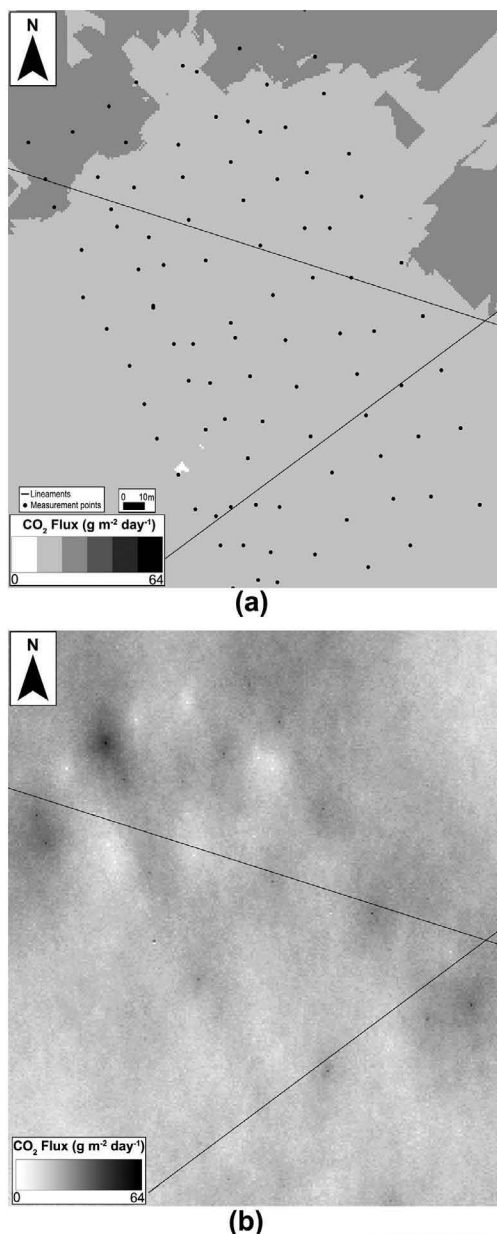


Fig. 15. (a) Surficial distribution of the diffuse soil CO₂ flux, in g m⁻² day⁻¹, for Leiva site (March 2010), by means of a kriging estimation. (b) Sequential Gaussian simulation of the surficial CO₂ flux.

4. The CO₂-rich deep saline aquifer sealed by Tertiary marls represents an excellent geological example to guarantee, by analogy, the long-term CO₂ storage, as long as the site would not anthropologically perturbed as it occurs at the Mazarrón-Gañuelas Tertiary Basin.

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